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ABSTRACT

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Detailed results are presented of a study of the interaction of powdered carbides (TiC, ZrC, HfC, NbC, TaC, Mo_2C, WC) nitrides (TiN, ZrN), and borides (TiB_2, ZrB_2, TaB_2) with solid Nb, Ta, Mo, and W held in contact at 900 to 2200°C for 2 or 5 hr in a vacuum. /167*

Data obtained by microscopic examination and microhardness measurements show that up to 1100°C none of the compounds tested reacts with refractory metals. Borides, which appear to be the most active, begin to react first, e.g., ZrB_2 with Nb at 1100°C and with W, Mo, and Ta at 1200°C; TiB_2 with Nb and Mo at 1200°C; and TaB_2 with W, Mo, Ta, and Nb at 1600°C. Carbides are more stable in contact with refractory metals: reactions between HfC and Nr or Ta, ZrC and Nb, and TaC and Nb begin at 1000°C; those between TiC and Nb; NbC and Nb, Ta, or Mo; Mo_2C and Ta, Mo,

*Numbers given in the margin indicate the pagination in the original foreign text.

or W; and WC and Ta begin at 1800°C. Along with TaC, which at 2200°C is stable in contact with Ta, the most stable compounds were found to be nitrides TiN and, especially, ZrN. Except for a reaction with Nb at 1800°C, TiN does not react at temperatures below 2000°C. ZrN reacts with Nb at 2000°C and with Mo at 2100°C but does not react with Ta or W even at 2100°C.

Author

The development of high-temperature technology is restricted in many cases by the lack of materials which are stable in contact with one another under these conditions. In particular, of considerable practical interest is the knowledge of the nature of the interaction between refractory compounds and refractory metals during mutual contact in the solid state at high temperatures. Information on this problem is very scarce (ref. 1) and has not been systematic; for this reason, the present study was undertaken.

A study was made of the behavior during heating of carbides (TiC, ZrC, HfC, NbC, TaC, Mo_2C and WC), nitrides (TiN, ZrN) and borides (TiB_2, ZrB_2 and TaB_2) held in contact with compact refractory metals (Nb, Ta, Mo and W) exposed in a vacuum to temperatures of 900-2200° for up to 5 hr.

Samples of refractory metals in the form of prisms or half-cylinders were pressed into carbide, boride or nitride powders in graphite dies (fig. 1). Assuming that the reaction of carbides with graphite occurs at very high temperatures, of the order of 3000° and higher (refs. 2 and 3), and that borides do not react with graphite either up to 2200-2300° (ref. 4), the samples of refractory metals were pressed in carbide and boride powders directly into graphite molds. However, in the case of nitrides, which readily react with graphite, the samples were pressed in molds lined with sheet tantalum or molybdenum. The "compacts" prepared in this manner were heated in a vacuum retort furnace (ref. 5) by passing the current directly through the mold and controlling the temperature with an optical pyrometer. After heating under a predetermined schedule, the compacts were furnace-cooled, the metal samples were extracted, and polished sections were prepared for subsequent microstructural analyses and microhardness measurements (under a 50 g load).[1]

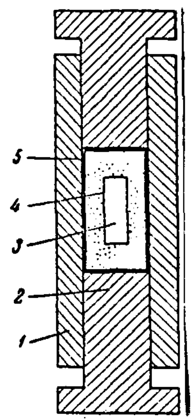

Figure 1. Diagram of the packing of samples in the die: 1, graphite matrix; 2, punch; 3, sample of refractory metal; 4, powder of refractory compound; 5, molybdenum or tantalum lining.

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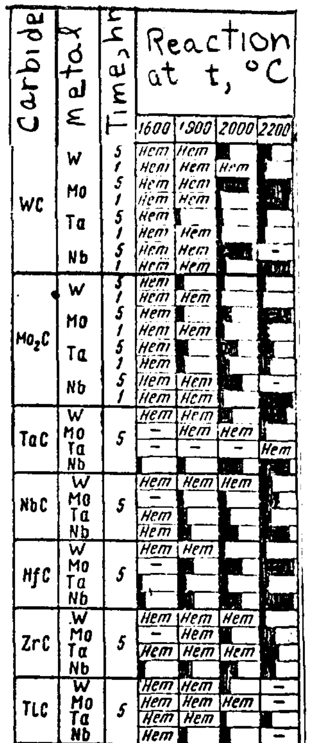
[1]In the original state, the metals studied had the following microhardness values (in kg/mm^2): Na, 195; Ta, 396; Mo, 276; W ~ 400.

Interaction with Carbides

Results of a visual study of the nature of the interaction between the refractory metals and carbides are given in figure 2, which shows that at 1600° almost all the metals are stable in contact with carbides except the pairs ZrC-Nb, HfC-Nb, HfC-Ta and TaC-Nb, during the 5 hr contact of which a slight interaction is observed (blackened areas of the columns in figure 2). At 1800°, this interaction becomes intensified, and an interaction is also seen to begin in the pairs TiC-Nb, HfC-Mo, NbC-Nb, NbC-Ta, NbC-Mo, Mo_2C-Ta, Mo_2C-Mo, Mo_2C-W and WC-Ta. At 2000°, a more or less active interaction is observed in all pairs except TiC-Ta, ZrC-Ta, ZrC-W, NbC-W, TaC-Mo and during brief contact in the WC-W pair. Finally, at 2200°, the most stable pair is TaC-Ta, while a relatively weak interaction is also observed in the pairs TiC-Ta, ZrC-Mo, HfC-Ta, HfC-W, TaC-Mo, Mo_2C-W and WC-Ta.

When TiC is in contact with Nb at 1800°, a phase is formed with a hardness of 3150 kg/mm^2 (the microhardness of TiC and NbC is respectively 3000 and 1960 kg/mm^2) at the boundary with niobium (fig. 3a), whereas at 2000° the microhardness of this phase rises to 3500 kg/mm^2 (table 1). Based on the data of reference 6, according to which the hardness in the system TiC-NbC changes without extrema, it is difficult to reach any definite conclusions concerning the nature of this phase. /168

When TiC is held in contact with Ta at temperatures up to 2000°, a phase is formed whose microhardness is 2400 kg/mm^2 (table 1), which corresponds to the hardness of the solid solution TiC-TaC with a content of 50 mol percent TaC. At 2200°, the hardness of the phase decreases to 1860 kg/mm^2; this is associated with an increase in TaC concentration in the solid solution to 80-85 mol percent. The rise in the TaC concentration in the solid solution TiC-TaC



NOTE: Hem = none.

Figure 2. Nature of the contact interaction between carbides and refractory metals at 1600-2200°.

with rising contact temperature of the TiC-TaC pair agrees well with the difference in the enthalpies of formation of TiC and TaC (the heat of formation of TiC is about twice as high as that of TaC).

In the interaction of TiC with W, which begins only at 2000°, a phase with a low microhardness (490 kg/mm^2) is formed which, according to the diagram of the pseudobinary system TiC-W (ref. 7), represents a solid solution of tungsten in TiC. In accordance with this diagram, one should expect a considerable interaction of TiC with W at lower temperatures as well, but at long exposures. Figure 3b shows the nature of the interaction between TiC and W at 2000° when the two are held in contact for 5 hr.

TABLE 1. MICROHARDNESS OF VARIOUS PARTS OF SAMPLES (a - center, b - edge, c - new phase) OF REFRACTORY METALS AFTER A 2- AND 5-HR CONTACT WITH CARBIDES.

Carbide	Metal	H_μ, kg/mm^2, portions of samples after contact at t, °C.											
		1600			1800			2000			2200		
		a	b	c	a	b	c	a	b	c	a	b	c
TiC	Nb	188±20*	194±23°	Нет	192*	452*	3136*	188±20	502±68	3535±890	—	—	—
	Ta	581±84	567±42	Нет	480±86	480±63	Нет	316±8	319±30	2123±376	362±26	367±29	1861±59
	Mo	308	286	Нет	291*	291*	Нет	289	248	Нет	—	—	—
	W	320	363	Нет	363*	352*	Нет	406	368	487	—	—	—
ZrC	Nb	282*	425*	2723*	240*	321*	2532*	236	281	3523	185*	477*	2556*
	Ta	561	591	Нет	516	635	Нет	661*	662*	Нет	592*	612*	1580*
	Mo	—	—	—	262	311	Нет	253*	339*	2509*	275*	326*	3693*
	W	411	362	Нет	314	414	Нет	328*	341*	Нет	499*	629*	4233*
HfC	Nb	177±23	264±28	4624±763	209±22	296±53	—	178±16	256±55	4254±343	182±7	216±31	3817±952
	Ta	345±13	363±29	—	322±20	343±24	—	236±14	268	—	202	217	—
	Mo	—	—	—	255	287	Нет	259	271	1870	268	280	1943
	W	512	673	Нет	543	672	Нет	609	570	3678	343	372	3415
NbC	Nb	247*	320*	Нет	298	321	—	269*	568*	—	264	620	—
	Ta	364*	359*	Нет	276*	352*	1904*	537*	656*	2541*	415*	577*	1888—3468
	Mo	194	221	Нет	196	261	362	206	306	726	217*	308*	1239*
	W	570*	564*	Нет	638*	592*	Нет	565	575	Нет	642*	541*	2350±59*
TaC	Nb	201	295	3442	225	317	4002	245	289	3302	187	296	3993
	Ta	—	—	—	—	—	—	—	—	—	366	342	Нет
	Mo	—	—	—	212	281	Нет	250	245	Нет	256	266	3347
	W	485	486	Нет	501	511	Нет	559	571	2091	424	528	3543

NOTE: Нет = none.

*Contact time, 2 hr.

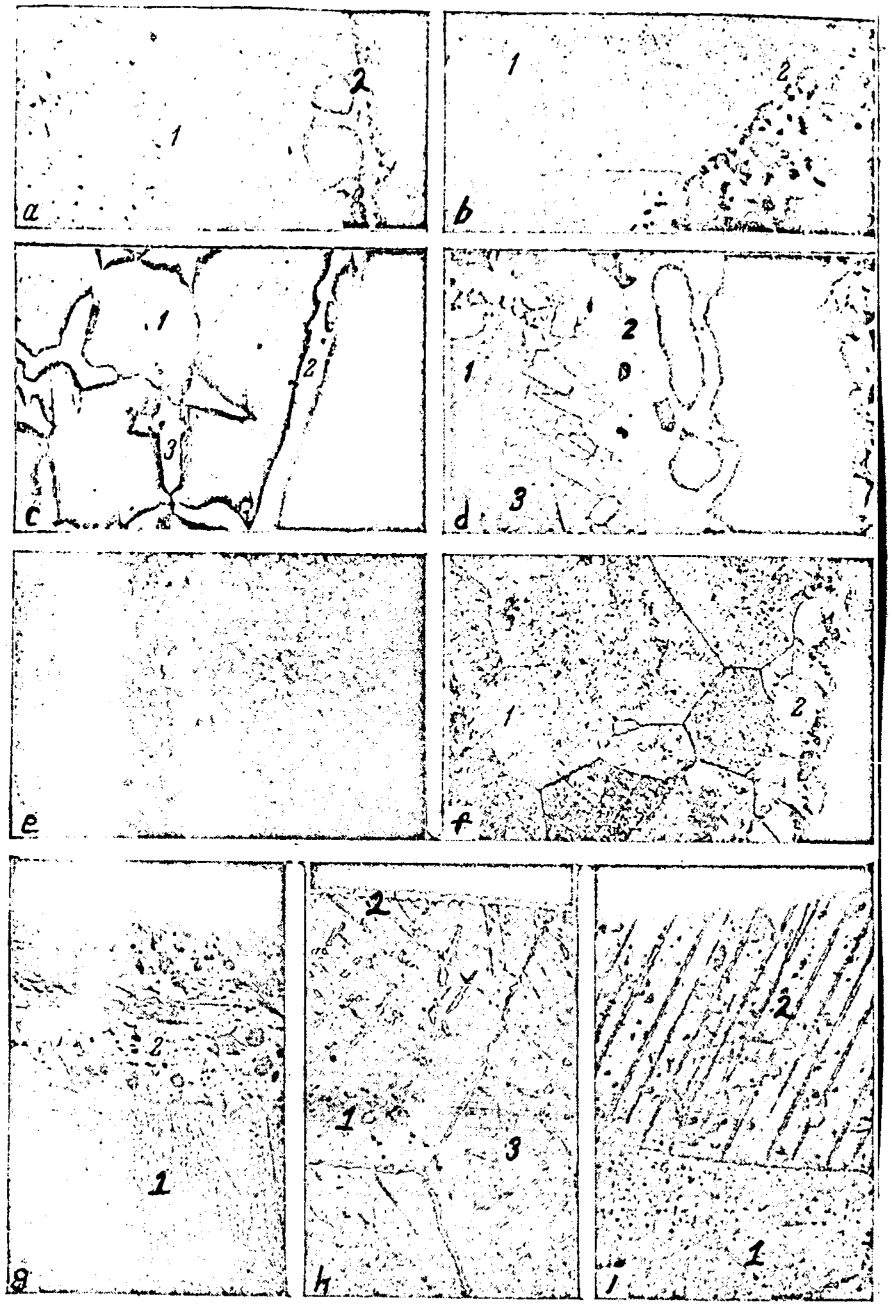


Figure 3. Microstructures of contact boundaries between refractory metals and carbides high temperatures after a 5-hr contact: a - Nb and TiC, 1800°, etching with $HF + HNO_3 + H_2O$ mixture (1 - Nb, 2 - new phase); b - W and TiC, 2200°, no etching (1 - W, 2 - reaction products); c - Nb and ZrC, 2000°, no etching (1 - Nb, 2 and 3 - new phase); d - Ta and ZrC, 2200°, no etching (1 - Ta, 2 and 3 - new phase); e - Mo and ZrC, 2000°, etching with H_2O_2 (1 - Mo, 2 - new phase); f - W and ZrC, 2200°, no etching (1 - W, 2 - new phase); g - Nb and HfC, 2000°, no etching (1 - Nb, 2 - layer); h - Ta and HfC, 2200°, etching with $HF + HNO_3 + H_2O$ mixture (1 - Ta, 2 and 3 - new phase); i - Mo and HfC, 2200°, etching with H_2O_2 (1 - Mo, 2 - layer); (x 200).

Zirconium carbide is slightly less stable in contact with refractory metals (fig. 2), particularly at high temperatures. It begins to react with niobium even at moderate temperatures to form a frontal layer of a phase which penetrates deep into the compact metal along the grain boundaries (fig. 3c) and has a hardness close to that of ZrC; apparently, this phase is the solid solution ZrC-NbC with a low concentration of the latter, as in the case of the solid solutions TiC-NbC (ref. 6). At the same time, the hardness of /171
niobium rises in the vicinity of the contact boundary because of the dissolution of excess carbon formed by the reaction ZrC + Nb → ZrC-NbC + C in niobium (table 1).

When ZrC is in contact with Ta, the reaction begins only at 2200° with the formation of tantalum monocarbide (the hardness of this phase is 1580, that of TaC, 1599 kg/mm^2), and the outer portion of the TaC layer peels off (fig. 3d). The hardness of tantalum increases markedly, apparently as a result of the dissolution of zirconium, which is set free during the contact reaction. Since the heat of formation of tantalum carbide is considerably less than that of zirconium carbide, the formation of TaC during the contact of ZrC with Ta is due to the substantial decrease in free energy upon dissolution of zirconium in tantalum; this agrees satisfactorily with the existence of a fairly wide region of solubility of zirconium in tantalum (ref. 8).

The reaction of ZrC with Mo begins at about 1900° with the formation of a phase whose hardness is close to that of ZrC; at 2200° this hardness increases considerably (table 1), apparently owing to the formation of a solid solution of zirconium and molybdenum carbides. The grains of this phase (fig. 3e) are round in a shape which resembles that of grains of the solid solution TiC-WC obtained by recrystallization through a cobalt melt (ref. 9). The hardness of the molybdenum remains practically unchanged (table 1), rising slightly only at the boundary with ZrC.

With tungsten, ZrC begins to react only at 2200° to form a frontal layer of a new phase (fig. 3f) having a high hardness; there is an appreciable increase in the hardness of tungsten itself (table 1). Hafnium carbide proved least stable in contact with refractory metals during heating (fig. 2). It reacts with niobium as low as 1600° to form a very hard phase whose microhardness decreases with rising contact temperature (table 1). This phase consists of a solid solution of hafnium and niobium monocarbides; in addition to being very hard, this phase is known to have high melting points. The solid solution forms on the surface of niobium in the form of a frontal layer (fig. 3g); at 2200°, the reaction between HfC and Nb practically proceeds to completion, and the excess carbon liberated by the reaction HfC + Nb → HfC-NbC + C forms characteristic spherical segregations in the layer of the solid solution.

With tantalum, hafnium carbide begins to react as low as 1600°, but the reaction is slow up to high temperatures (fig. 3h), forming a narrow frontal layer and involving a partial penetration of the new phase into the tantalum sample. Measurements of the microhardness of this phase have been unsuccessful. The hardness of tantalum obviously increases owing to the dissolution of carbon therein.

The interaction of HfC with molybdenum proceeds vigorously (fig. 3i), with the formation of a frontal layer of a new phase (solid solution of carbides) having a hardness of 1800-1900 kg/mm^2. It is possible that this phase consists of a solid solution of molybdenum in hafnium carbide, similar to the solid solution of WC in TiC. This is supported by the fact that the hardness of molybdenum remains practically unchanged (table 1); this would not occur during the formation of a solid solution of carbides and the formation of free carbon, which would dissolve in molybdenum and thus necessarily raise its hardness.

The least extensive reaction of HfC is observed with tungsten; it is associated with the formation of a phase with a hardness of 3400-3600 kg/mm^2 and a substantial increase in the hardness of tungsten.

Like hafnium carbide, niobium carbide is not very stable when heated /172 in contact with refractory metals (fig. 2).

When NbC reacts with niobium, the formation of an outer layer of a new phase is not observed up to 2000°; starting at 2000° and above, a thin layer is observed whose hardness cannot be measured. The hardness at the center of the niobium sample remains practically unchanged (fig. 4), and the hardness of the edge increases regularly, apparently owing to the formation of a solid solution of carbon. Hence, it may be assumed that the phase forming on the surface of the contact consists of the lower niobium carbide Nb_2C.

The reaction of NbC with tantalum begins at 1800° and is somewhat enhanced as the temperature rises. The hardness of the layer formed at 1800° is 1900 kg/mm^2, which is close to the hardness of the solid solution Nb_2C-Ta_2C with an approximately equimolar concentration of the components. At 2000°, the hardness

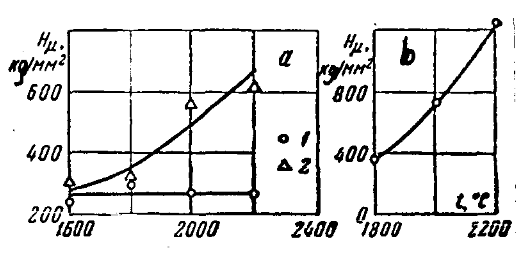


Figure 4. Effect of temperature of contact with NbC on the microhardness of the center (1) and edge (2) of niobium sample (a) and also of the phase formed in molybdenum under these conditions (b).

of the new phase becomes approximately 2500 kg/mm^2, and at 2200°, double layers are formed (fig. 5a), the layer adjoining tantalum having a hardness of 1890, and the outer layer, a hardness of about 3470 kg/mm^2; at the same time, the hardness of tantalum increases (table 1).

When NbC is in contact with molybdenum at high temperatures, the reaction begins at 1800° with the formation of a porous layer of a phase (fig. 5b) whose hardness increases monotonically with the temperature (fig. 4b), reaching values close to the hardness of Mo_2C and MoC (about 1500 kg/mm^2). At the same time, the hardness of molybdenum increases substantially owing to the dissolution of carbon therein.

Niobium carbide reacts with tungsten only beginning at 2200°; the phase thus formed has a high microhardness (table 1). Its nature is at yet unclear; a characteristic feature of this phase is its deep penetration into the tungsten sample (fig. 5c).

With niobium, tantalum carbide begins to react at 1600° (fig. 2), i.e., at lower temperatures than NbC reacts with Ta; a phase is formed at once which has a very high hardness (table 1). After contact at 1800-2200°, this hardness becomes about 4000 kg/mm^2, which is close to the hardness of the phase formed after contact between NbC and Ta at 2200°. The hardness of niobium at the contact surface increases by a factor of 1.5 and changes little with rising temperature. The new phase constitutes a broad and well-formed layer (fig. 5d).

With tantalum, TaC does not react even at 2200°; this is due primarily to a considerably smaller heat of the reaction of formation of Ta_2C (15.5 kcal/mol) as compared to TaC (36 kcal/mol), which renders the reaction between Ta and TaC improbable.

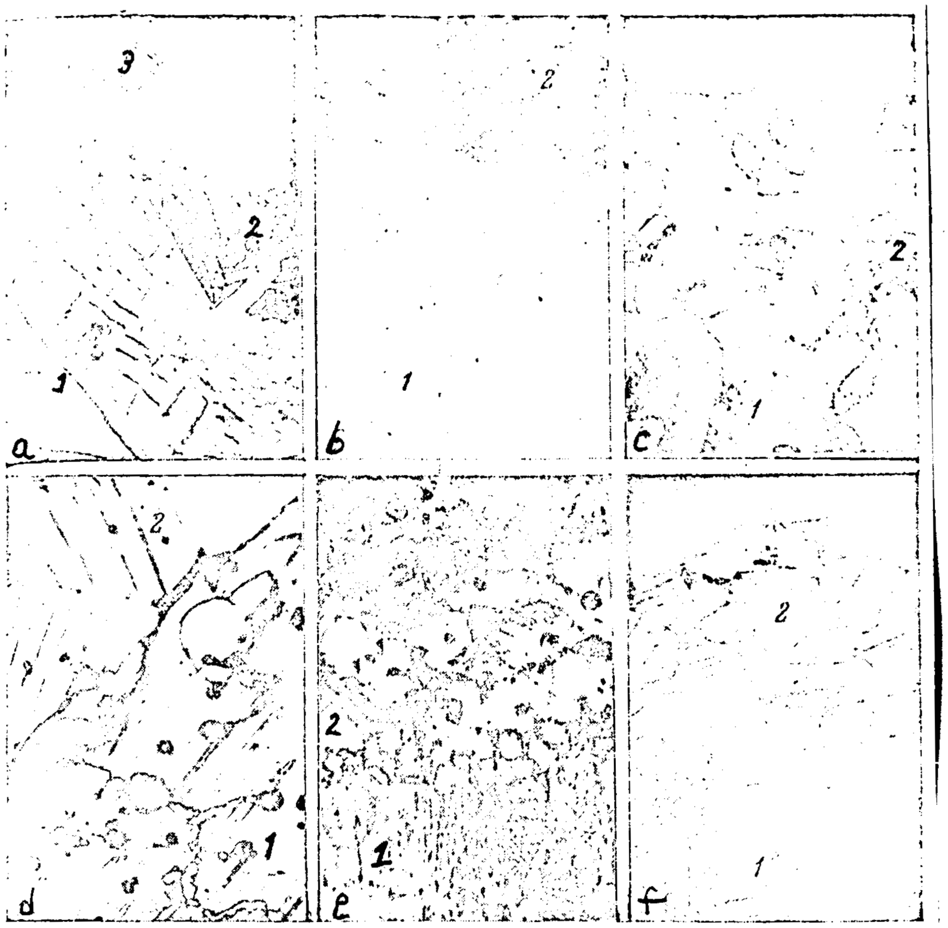


Figure 5. Microstructures of contact boundaries between refractory metals and carbides at high temperatures after 5 hr: a - Ta and NbC, 2200°, etching with HF + HNO_3 + H_2O mixture (1 - Ta, 2 and 3 - new phases); b - Mo and NbC, 1800°, etching with H_2O_2 (1 - Mo, 2 - new phase); c - W and NbC, 2200°, no etching (1 - W, 2 - new phase); d - Nb and TaC, 2200°, etching with HF + HNO_3 + H_2O mixture (1 - Nb, 2 - new phase); e - Mo and TaC, 2200°, etching with H_2O_2 (1 - Mo, 2 - new phase); f - W and TaC, 2200°, etching with H_2O_2 (1 - W, 2 - new phase); (× 200).

With molybdenum, tantalum carbide begins to react at 2200°; the phase thus formed is very hard (table 1) and the hardness of molybdenum both at the center and at the edge of the sample remains practically unchanged. The layer formed is porous (fig 5e). When TaC reacts with tungsten, a dense layer of a new phase is formed (fig. 5f) with a hardness of about 3500 kg/mm^2; at the same time, the hardness of tungsten increases appreciably (table 1). Since according to the data of reference 6 the hardness of the phases in the system TaC-WC does not exceed 1800 kg/mm^2, it may be assumed that the high hardness of the phases /17 resulting from the reaction of TaC with Mo and W is due to the formation of complex ternary phases of the systems Ta-Mo-C and Ta-W-C.

Reaction with Nitrides

As follows from the data shown in figure 6, titanium and zirconium nitrides behave in a relatively stable manner in contact with refractory metals at high temperatures; this is particularly true of zirconium nitride. Both nitrides are least stable in contact with niobium.

Carbide	Metal	Time, hr	Reaction at t, °C			
			1600	1800	2000	2100
ZrN	W	5	—	—	Hem	Hem
		2	—	—	—	Hem
	Mo	5	—	Hem	Hem	
		2	—	Hem	Hem	Hem
	Ta	5	—	—	Hem	Hem
		2	—	—	Hem	Hem
	Nb	5	—	—		
		2	—	—		
TiN	W	5	—	Hem		
		2	Hem	Hem		
	Mo	5	—	Hem		
		2	Hem	Hem		—
	Ta	5	—	Hem	—	
		2	Hem	—		—
	Nb	5	—			
		2	—	—		

NOTE: Hem = none

Figure 6. Nature of contact interaction between nitrides and refractory metals at 1600-2100°.

The reaction of titanium nitride with niobium is already appreciable at 1800°, and at 2100° almost all the niobium converts into new phases. At 1800° (5 hr) and 2000°, a homogeneous phase is formed (fig 7a) with a hardness of 1800-2100 kg/mm^2 (table 2), which apparently corresponds to a solid solution of titanium nitride and niobium nitride (TiN-NbN). At 2100°, a layer of a phase is formed having a hardness which changes with the contact time: 1250 (2 hr), 1600 (5 hr), and 1950 kg/mm^2 (8 hr). It may be assumed that when the contact /174

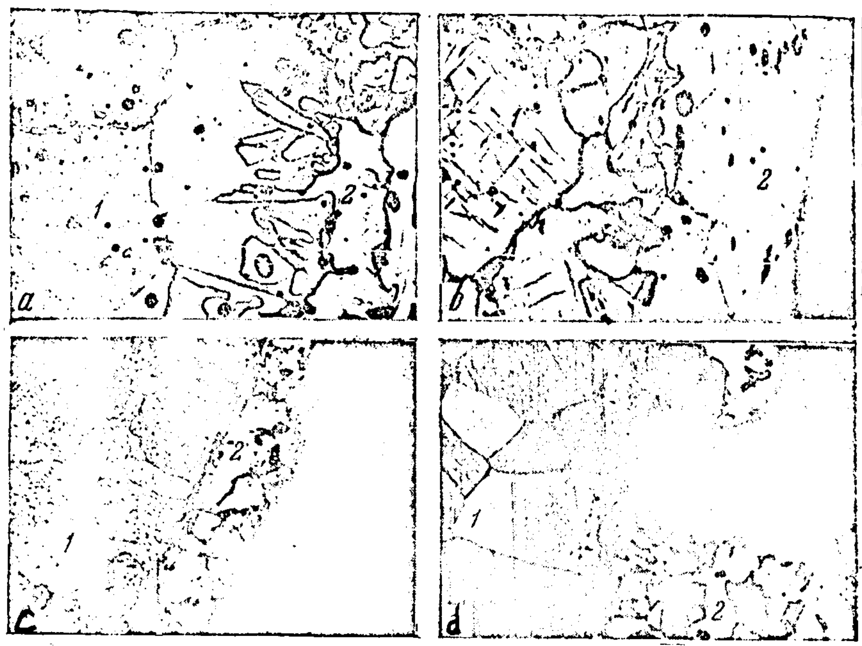


Figure 7. Microstructures of contact boundaries between refractory metals and nitrides at high temperatures after 2-5 hr: a - Nb and TiN, 2000°, 5 hr, no etching (1 - Nb, 2 - new phase); b - same, 2100°, etching with HF + HNO_3 + H_2O mixture; c - Ta and TiN, 2000°, 2 hr, etching with HF + HNO_3 + H_2O mixture (1 - Ta, 2 and 3 - new phases); d - Mo and TiN, 2100°, 3.5 hr, etching with H_2O_2 (1 - Mo, 2 - TiN); (x 200).

TABLE 2. MICROHARDNESS OF VARIOUS PORTIONS OF SAMPLES (a - center, b - edge, c - new phase) OF REFRACTORY METALS AFTER CONTACT WITH NITRIDES.

Carbide	Metal	Time, hr	H_μ, kg/mm², portions of samples after contact at t, °C											
			1600			1800			2000			2100		
			a	b	c	a	b	c	a	b	c	a	b	c
TiN	Nb	2	—	—	—	—	—	—	200±56	481±17	1820±180	253±10	355±35	1251±129
		5	—	—	—	273	395	2220	232±12	421±7	2116±262*	253±10	305±10	1591±200
	Ta	2	215±12	487±42	Нет	—	—	—	441±8	556±17	867±69*	—	—	—
		5	—	—	—	458	412	Нет	—	—	—	502±11	490±14	2339±129
	Mo	2	215±6	223±8	Нет	205±8	201±3	Нет	243±6	305±67	Нет	235±9	289±24	Нет
		5	—	—	—	—	—	—	—		—	226±16	263±11	2009±16**
	W	2	—	—	—	522±15	622±26	Нет	497	525	Нет	403	403	—
		5	—	—	—	470±13	457±5	Нет	442±23	550±26	1976±149**	—	—	—
ZrH	Nb	2	—	—	—	—	—	—	172±24	470±34	750±86***	—	—	—
		5	—	—	—	—	—	—	276±11	202±11	223±217	329±28	475±17	2081±35
	Ta	2	—	—	—	—	—	—	391±14	470±23	Нет	437±9	491±9	Нет
		.5	—	—	—	—	—	—	343±27	444±29	Нет	382	382	Нет
	Mo	2	—	—	—	—	—	—	236±10	239±15	Нет	230	243	Нет
		5	—	—	—	229	233	Нет	210±6	244±6	Нет	251	305	2814
	W	2	—	—	—	—	—	—	469	545	Нет	438±14	471±33	Нет
		.5	—	—	—	—	—	—	504±24	461±18	Нет	501	462	Нет

NOTE: HeT = none.

*Hardness inside grain; external portions have a hardness of 2383 ± 128 (in contact with Nb) and 2317 ± 226 kg/mm² (in contact with Ta).

**Contact time 3.5 hr.

***In addition, 2005 ± 120 and 2138 ± 226 kg/mm².

time is short at 2100°, this layer consists of the nitride NbN (according to the data of ref. 10, the hardness of NbN is 1396 kg/mm^2) with a certain deficiency of nitrogen; after 5 hr it consists of the nitride Nb_2N (hardness 1720 kg/mm^2) and after longer periods, of a solid solution of TiN in Nb_2N. The layer formed after 5 hr at 2100° is dense and adheres well to niobium (fig. 7b).

With tantalum, titanium nitride begins to react during the first two hours of contact at 2000°; it may be that the temperature of the start of the reaction is even lower. At 2000°, double layers are formed (fig. 7c); the layer adjoining tantalum has a low hardness of about 870 kg/mm^2 (apparently a layer deficient in nitrogen and consisting of the nitride TaN),[1] and the outer layer has a hardness of 2300 kg/mm^2 and consists of a solid solution of tantalum nitride and titanium nitride (or, more probably, of a ternary chemical component of the system Ta-Ti-N).

When titanium nitride is held in contact with molybdenum, a slight but visible reaction begins at 2000° and ends mainly in the dissolution of nitrogen in molybdenum, as indicated by an increase in the hardness of the latter (table 2). No new chemical compounds are formed during the contact heating, which is in agreement with the thermodynamic instability of molybdenum nitrides (ref. 1); the titanium nitride powder around the molybdenum sample (fig. 7d) sinters, and its hardness within the limits of experimental error remains equal to the hardness of titanium nitride (ref. 10).

With tungsten, the reaction of titanium nitride begins at 2000° and proceeds more extensively than with molybdenum, but, as in the case of the latter, is limited by the formation of a solid solution of nitrogen in tungsten, the hardness of titanium nitride remaining the same.

[1]The hardness of TaN given by reference 10 is 1060 kg/mm^2.

Experiments on the interaction of niobium with titanium nitride containing insufficient nitrogen (i.e., in the region of homogeneity of the Ti-N phase) have shown that this interaction is enhanced as the nitrogen content of titanium nitride decreases.

When zirconium nitride reacts with niobium at all of the temperatures studied, a broad layer of reaction products is observed on the niobium samples; on the basis of their hardness, these products represent ternary phases of the system Zr-Nb-N.

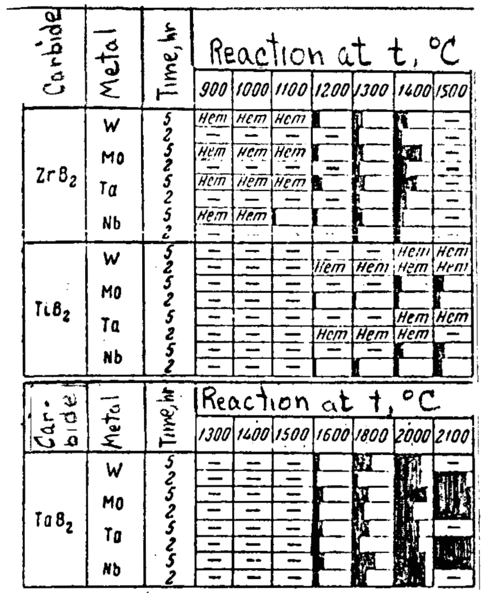
The reaction of zirconium nitride with tantalum is limited by a certain dissolution of nitrogen in tantalum (table 2), which corresponds to the absence of stable ternary chemical compounds in the Zr-Ta-N system.

On the contrary, the reaction of zirconium nitride with molybdenum at 2100° results in the formation of a new phase with a hardness of 2800 kg/mm^2, which is twice that of ZrN and four times that of MoN.

In the ZrN-W system, no reaction is observed even at high /176 temperatures if a certain dissolution of nitrogen in tungsten is not considered.

Interaction with Borides. As can be seen from figure 8, titanium diboride (TiB_2) is most stable in contact with refractory metals at high temperature; zirconium boride (ZrB_2) is slightly less stable. TaB_2 displays a low stability, but at high temperatures, when titanium and zirconium diborides react very actively with refractory metals.

Table 3 lists data on the microhardness for the phases formed /177 when ZrB_2 is held in contact with refractory metals at high temperatures. In all cases, borides of the corresponding refractory metals and their solid solutions with zirconium boride are formed, while at the same time boron dissolves in the refractory metals.



NOTE: Hem = none.

Figure 8. Nature of contact interaction between borides and refractory metals at 900-2100°.

TABLE 3. MICROHARDNESS OF VARIOUS PORTIONS OF SAMPLES (a - center, b - edge, c - new phase) OF REFRACTORY METALS AFTER CONTACT WITH ZrB_2

Metal	Time, hr	H_μ, kG/mm², portions of samples after contact at t, °C: 1200 a	1200 b	1200 c	1300 a	1300 b	1300 c	1400 a	1400 b	1400 c
Nb	2	—	—	—	155±8	207±16	2491±188	102±1	131±9	3260±111
	5	172±12	242±10	2864±321	131±12	210±11	2717±291	202±6	196±5	3487±237
Ta	2	—	—	—	383±23	383±23	2595±170	407±9	469±18	3183±235
	5	440±11	492±9	2205±190	426±28	474±8	2666±74	439±17	412±24	2973±320
Mo	2	—	—	—	247±19	254±29	3065±167	221±7	236±7	2814±50
	5	262±5	272±17	2106±15	229±9	244±11	2734±159	228±5	239±3	2494±10
W	2	—	—	—	519±22	522±16	3018±305	477±28	516±26	2353±242
	5	529±13	552±22	3357±153	567±15	532±20	2963±103	528±11	551±16	2795±245

Figure 9 shows the temperature dependence of the thickness of the layers formed when ZrB_2 is held in contact with refractory metals for 5 hours. On the basis of these data, an estimate was made of the coefficients of reaction diffusion during the reaction of zirconium boride with these metals, and the corresponding activation energies were evaluated (table 4). Since in ordinary diffusion one should expect a rise in the activation energy in passing /178

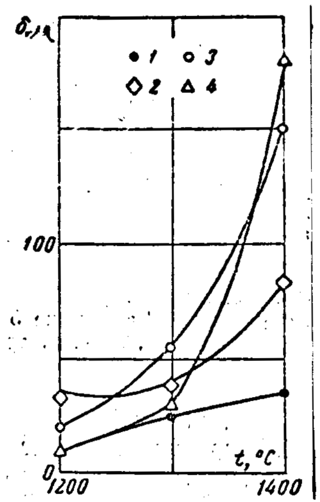


Figure 9. Effect of temperature of contact between ZrB_2 and refractory metals (1 - Nb, 2 - W, 3 - Ta, 4 - Mo) on the thickness of layers formed, δ, μ.

TABLE 4. EFFECT OF TEMPERATURE OF CONTACT BETWEEN ZrB_2 AND REFRACTORY METALS ON THE THICKNESS OF LAYERS FORMED, COEFFICIENT OF REACTION DIFFUSION, AND ACTIVATION ENERGY.

METAL	t, °C	Time, hr	δ, μ	$D \cdot 10^{-10}$, cm^2/sec	Q, kcal/mol	D_0, cm^2/sec	Metal	t, °C	Time, hr	δ, μ	$D \cdot 10^{-10}$, cm^2/sec	Q, kcal/mol	D_0, cm^2/sec
Nb	1200	5	10	0.14			Mo	1200	5	10	0.14		
	1300	2	9	0.28				1300	2	15	0.80		
	1300	5	27	1.00	~70	0.46		1300	5	30	1.20	~124	$3.1 \cdot 10^7$
	1400	2	30	3.00				1400	2	100	35.00		
	1400	5	36	1.80				1400	5	180	45.00		
Ta	1200	5	20	0.56			W	1200	5	35	1.70		
	1300	2	30	3.00				1300	2	30	3.10		
	1300	5	55	4.20	~97	$2.0 \cdot 10^4$		1300	5	40	2.20	~ 63	0.25
	1400	2	90	30.00				1400	2	44	6.70		
	1400	5	150	31.00				1400	5	84	9.80		

from the less to the more refractory metals, the data obtained, which do not behave in this manner, indicate the nature of the phases formed and their thermodynamic stability.

These results show that when ZrB_2 reacts with Nb, Ta and W, mainly solid solutions of borides are formed; with molybdenum, ternary chemical compounds Zr-Mo-B are formed with crystal structures different from the structure of molybdenum and from that of ZrB_2; the formation of these compounds involves a complete rearrangement of the crystal lattices of the phases in contact.

Tantalum boride paired with niobium begins to react appreciably (fig. 8) as low as 1600° to form a phase which can be identified as TaB based on its microhardness (table 5); after longer exposures at 1600° and also at higher temperatures, a frontal layer of a phase close in hardness to NbB_2 is formed, and at 2000° and higher, the hardness of the phase on the niobium samples decreases again, while practically all of the niobium enters into the reaction.

With tantalum, TaB_2 reacts less extensively (fig. 8); it begins to react at 1600° to form the phase Ta_3B_4, and the phase Ta_3B_2 is formed at 1800°. At 2000°, two layers are formed on tantalum, an outer layer of Ta_3B_2 (columnar crystals shown in figure 10a) and an inner layer adjoining tantalum and having a hardness of 2170 kg/mm^2, which is below the hardness of Ta_3B_2. The latter phase appears to consist of the lower tantalum boride Ta_2B (ref. 11).

Since the hardness of borides is determined within the limits of each given Me-B system by the character of the structural elements of boron atoms and decreases (fig. 11) when these elements are simplified (ref. 11), it should be expected that the conversion from the Ta_3B_2 phase to the Ta_2B phase and further to metallic tantalum or, more accurately, to a solid solution of boron in tantalum will occur with a monotonic change in microhardness /180 which can be roughly approximated by a straight line.[1]

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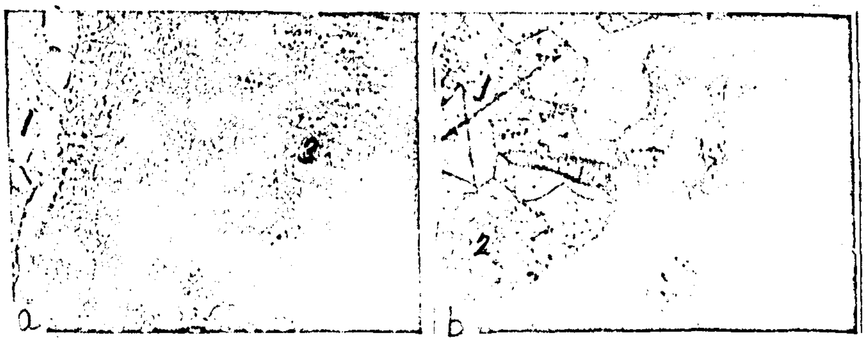

Figure 10. Microstructures of contact boundaries between tantalum and TaB_2 and molybdenum and TaB_2 at 2000° after 5 hr: a - Ta, no etching (1 - Ta, 2 - Ta_2B, 3 - Ta_3B_2); b - Mo, etching with H_2O_2 (1 - Mo, 2 - Mo_2B); (X 200).

In addition, the phase with a hardness of 2170 kg/mm^2, formed in direct contact with tantalum at 2000°, should correspond to a boron content (see fig. 11) of approximately 2.7 percent, which is in good agreement with the boron content in the Ta_2B phase (2.9 percent). The extreme left point on the curve, located on the hardness axis, corresponds to the hardness of a solid solution of boron in tantalum, which, judging from the data in table 5, is formed at all temperatures of contact between TaB_2 and tantalum.

When TaB_2 reacts with molybdenum, the reaction begins as low as 1600°, and at 2100° almost the entire sample enters into it. Up to 2100°, this phase, which forms a layer penetrating deep into the molybdenum sample in

[1]This monotonicity should take place only for similar structural elements made up of boron atoms in boride structures: double chains (Me_3B_4), single chains (MeB), paired boron atoms (Me_3B_2) and single mutually isolated atoms (Me_2B). For this reason, the hardness of MeB_2, which has networks of boron atoms with a distinct separation of the structural elements consisting of boron atoms and metal atoms, should not obey this general relationship.

TABLE 5. MICROHARDNESS OF VARIOUS PORTIONS OF SAMPLES (a - center, b - edge, c - new phase) OF REFRACTORY METALS AFTER CONTACT WITH TaB_2.

Metal	Time, hr	H_μ, kg/mm², portions of samples after contact at t, °C											
		1600			1800			2000			2100		
		a	b	c	a	b	c	a	b	c	a	b	c
Nb	2	172±12	190±12	3004±121	136±7	187±10	2404±24	136±16	173±9	3052±87	—	—	—
	5	151±1	186±13	2625±114	266±26	373±22	2638±193	163±7	235±69	1712±421	—	—	—
Ta	2	485±8	474±32	2858±420	465±29	460±32	2887±244	440	445±21	2381±32	—	—	—
	5	436±24	455±16	3373±314	410±51	462±6	2750±112	443±17	484±13	2164±46*	—	—	—
Mo	2	261±8	256±7	3192±292	210±7	220±5	1737±74	220±5	227±10	2216±120*	—	—	—
	5	273±15	283±10	2504±89	232	223	2584	232±8	234±37	2354±290	232±4	224±15	1795±285*
W	2	499±24	477±21	3154±178	—	—	—	403±18	463±11	1980±90	473±3	443±6	3466±241*
	5	515±13	527±15	3353±137	—	—	—	446±12	446±12	2998±255	—	—	—

*Hardness inside grain; outer portions of a hardness of 2856 ± 124 (in contact with Ta), 2118 ± 31 (in contact with Mo, 2 hr), 1290 ± 107 (in contact with Mo, 5 hr) and 2749 ± 340 kg/mm² (in contact with W).

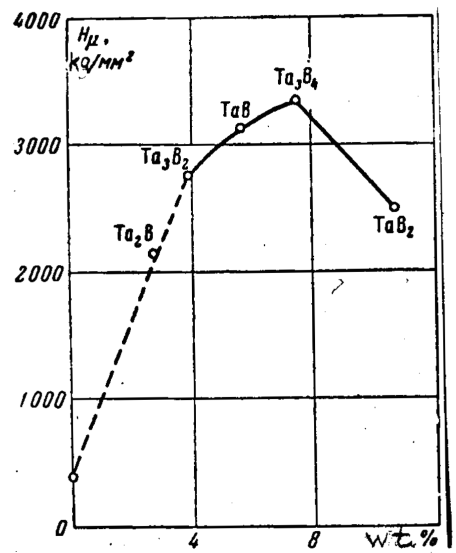

Figure 11. Hardness of tantalum boride vs. boron content.

certain areas (fig. 10b), consists of Mo_2B; at 2100°, according to the phase diagram of the Mo-B system (ref. 11), this phase decomposes to form mainly MoB.

The reaction between TaB_2 and tungsten begins at 1600° with the formation of the α-WB phase up to 2100°, and at 2100° two layers are formed: one, α-WB, adjoining the tungsten layer, and an outer layer whose hardness is close to that of W_2B_5.

Summary

1. The nature of the interaction of metallike carbides (TiC, ZrC, HfC, NbC, TaC, Mo_2C and WC), nitrides (TiN and ZrN) and borides (TiB_2, ZrB_2 and TaB_2) held in contact with refractory metals (Nb, Ta, Mo and W) at temperatures up to 2100-2200° was investigated, and preliminary assumptions were made concerning the nature of the phases thus formed and causes of their formation.

2. Borides were least stable in contact with refractory metals at high temperatures; nitrides and certain carbides were more stable. No interaction

involving the formation of new chemical compounds is observed at 2200°, only in the case of contact between TaC and Ta and at 2100° between zirconium nitride and Ta and also W.

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